Polymer Membranes

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Reverse Osmosis

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Dialysis and reverse osmosis

Dialysis is a separation process with increasing areas of application in clinical, biochemical and environmental analysis. A donor and an acceptor solution are separated by a semipermeable membrane (**Figure 1**).

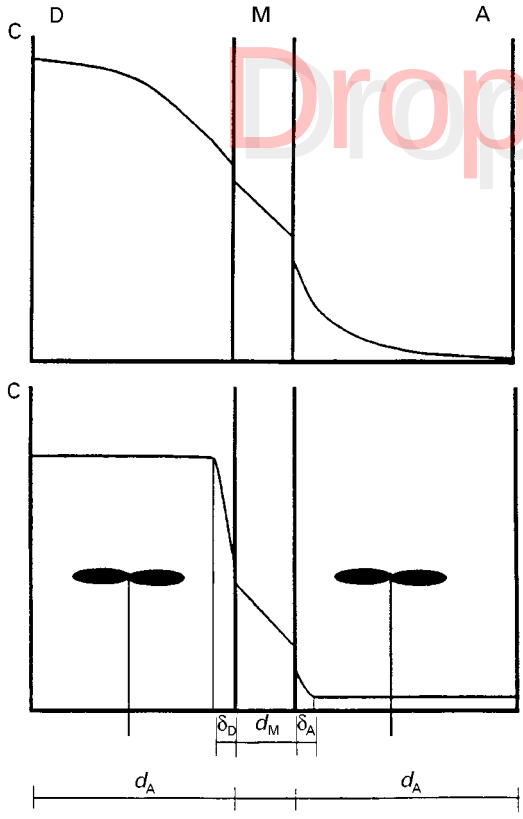

Figure 1 Dialysis between quiescent and stirred solutions. C, concentration; D, donor solution; A, acceptor solution; M, membrane; d_A, d_D and d_M; thicknesses of the corresponding phase layers, δ_A and δ_D; thicknesses of the diffusional boundary layers.

When the solutions have different solute activities a diffusional membrane transport from the more to the less concentrated solution takes place to establish the thermodynamic equilibrium. In most applications mass transfer to and away from the separation membrane is accelerated convectively by stirring or by the use of flow-through separation cells.

When the solutions have different solvent activities an osmotic pressure is built up, which causes a solvent flow to the solution of the lower solvent activity. This process is termed osmosis. Reverse osmosis is defined as a process during which an outer pressure is applied to force the solvent through a membrane, which is permeable to the solvent and rejects the solute. Reverse osmosis is applied to purify water for laboratory use and is very promising as a preconcentration technique in trace and environmental analysis.

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Fundamentals

Thermodynamic Aspects

During dialysis the activities of the solute i in the donor and the acceptor solutions differ. The difference between the chemical potentials $\mu_{i,D}$ and $\mu_{i,A}$ is the free enthalpy per mole, which propels the dialysis. The dialysis finishes when the thermodynamic equilibrium shown in eqn [1] is reached:

$$\mu_{i,D} = \mu_{i,A} \qquad [1]$$

The equilibrium constant K_i^* depends on the activity coefficients $f_{i,D}$ and $f_{i,A}$ and the absolute temperature T according to eqn [2]:

$$K_i^* = \frac{a_{i,A}}{a_{i,D}} = \frac{f_{i,A} \times c_{i,A}}{f_{i,D} \times c_{i,D}} = \exp\left[\frac{\mu_{i,D}^0 - \mu_{i,A}^0}{RT}\right] \qquad [2]$$

where $\mu_{i,D}^0$ and $\mu_{i,A}^0$ are the chemical potentials of the solute under standard conditions. c is concentration and a is activity. R is the molar gas constant. An effective separation ratio K_i, which is defined

according to eqn [3], is of analytical interest:

$$K_i = \frac{c_{i,A}}{c_{i,D}} \quad [3]$$

The activity coefficients f_i depend on the solvent, the ionic strength $I = \Sigma z_j c_j$ of the solution and the concentrations of all nondissociated solutes. The general index, j, labels the ions in the system with the electric charge z_j. Because in most cases:

$$\mu^0_{i,D} - \mu^0_{i,A} = 0 \quad [4]$$

it follows that:

$$K^*_i = 1 \quad [5]$$

and:

$$K_i = \frac{f_{i,D}}{f_{i,A}} \quad [6]$$

K_i differs from unity when the dialysis equilibrium is coupled to other equilibria and/or the activity coefficients $f_{i,D}$ and $f_{i,A}$ are different. Without coupled pushing and trapping reactions the enrichment E and the purification factor P can be calculated according to eqns [7] and [8]:

$$E = \frac{c_{i,A}}{c_{i,D,0}} = \frac{(c_{i,D,0} - c_{i,D})V_D/V_A}{c_{i,D,0}} \quad [7]$$

$$P = \frac{c_{i,D,0} - c_{i.D}}{c_{i,D,0}} = \frac{(c_{i,A} - c_{i,A,0})V_A/V_D}{c_{i,D,0}} \quad [8]$$

where $c_{i,D,0}$ and $c_{i,A,0}$ are the initial solute concentrations in the donor and in the acceptor solution, respectively, and V_A and V_D are the volumes of the corresponding solutions. The maximum enrichment factor is around 0.5 for $V_A \leq V_D$. The purification factor increases up to unity with the increasing ratio of V_A to V_D.

The chemical activities of the solvent are equal at dialysis equilibrium. According to eqn [9]:

$$\mu_{L,D} = \mu_{L,A} \quad [9]$$

and because:

$$\mu^0_{L,D} = \mu^0_{L,A} \quad [10]$$

it follows for the solvent L that:

$$K^*_L = \exp\left[\frac{1}{RT}\{V_{L,D}\pi_D - V_{L,A}\Pi_A\}\right] \quad [11]$$

where $V_{L,D}$ and $V_{L,A}$ are the partial molar volumes of the solvent which are equal to V_L for dilute solutions, and π refers to the osmotic pressure. It therefore follows that:

$$K^*_L = \exp\left[\frac{V_L}{RT}(\pi_D - \pi_A)\right] \quad [12]$$

with the osmotic pressure difference $\pi = \pi_D - \pi_A$. A volume change is effected to equilibrate the donor and the acceptor solutions. π can be calculated for every solution according to eqn [13]:

$$\pi = -(RT/V_L)\ln a_{x,L} \quad [13]$$

where $a_{x,L}$ is the activity $(x_L \cdot f_L)$ of the solvent with respect to the mole fraction x_L of the solvent. Therefore the osmotic pressure difference π has to be taken into consideration to calculate precisely almost all dialysis equilibria. The osmotic pressure difference causes a solvent flow through the separation membranes up to the state at which the hydrostatic backpressure compensates for the osmotic pressure. e.g. in the batch-type arrangement shown in **Figure 2**. If the pressure p_h is greater than the osmotic pressure the osmosis will be reversed. This reverse osmosis reaches an equilibrium, which can be described by eqn [14]:

$$K^*_L = \exp\left[\frac{V_L}{RT}(\pi - p_h)\right] \quad [14]$$

Obviously the equilibrium constant decreases with increasing pressure p_h. When the solute is rejected by the membrane it can be enriched in the donor solution.

To take into consideration the electric charges z_i of the solutes and of the separation membrane the Donnan effect has to be considered. The chemical potential μ_i is extended by a term for the electric potential gradient, ϕ. When a membrane separates

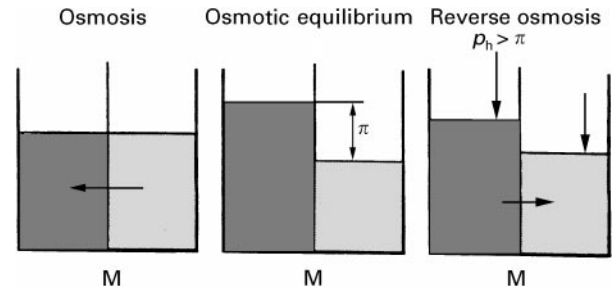

Figure 2 The principles of osmosis and reverse osmosis. M, membrane; p_h, outer pressure; π, osmotic pressure difference. ■, Aqueous salt solutions; □, water.

two solutions of a dissociating salt BA and one solution contains a rejected ion X^-, an electric potential difference $\phi = \phi_D - \phi_A$ is built up between the solutions. This Donnan potential influences the effective separation ratio K. The equilibrium constant is shown in eqn [15] with the Faraday constant **F**:

$$K_i^* = \exp[(\phi_D - \phi_A)z_i\mathbf{F}/RT] \qquad [15]$$

where F is the membrane area that is in contact with the solutions.

An outer electrical voltage U generates an electromigration of the anions to the positively charged anode and of the cations to the negatively charged cathode (**Figure 3**). The process is termed electrodialysis. If the potential difference between the electrodes U is smaller than the voltage U_D of the water decomposition a new electrochemical equilibrium is built up with the constant shown in eqn [16]:

$$K_i^* = \exp[(\phi_D - \phi_A + U)z_i\mathbf{F}/RT] \qquad [16]$$

In many practical applications the dialysis equilibrium is coupled with chemical equilibria, e.g. acid–base, redox, complexation and precipitation equilibria. It should be noted that distribution equilibria between two different solvents and phases can also be exploited to shift the overall distribution ratio K_i between the donor and acceptor solutions. The enrichment factor E can be increased by several orders of magnitude. The thermodynamics of the separation processes enable the attainable maxima of the enrichment and the purification factors to be estimated.

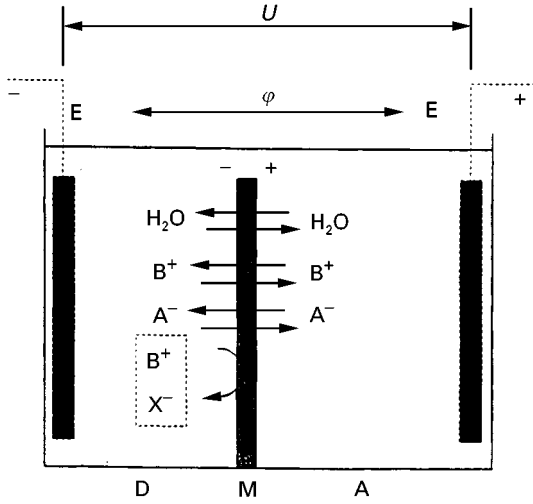

Figure 3 Domain dialysis across a microporous membrane. ϕ, Donnan potential; E, electrodes; U, outer voltage.

Mass Transport

Dialysis For quiescent donor and acceptor solutions the equilibration time ranges from minutes to several hours and is dependent on the geometrical size of the donor and acceptor chambers and the membrane permeability. In this case the equilibration is dominated by the slow diffusional analyte transport. The equilibration can be accelerated by convective mass transport according to Figure 1. Intensive stirring of both the acceptor and the donor solutions establishes diffusional boundary layers of thickness δ on the membrane. The diffusional boundary layer can also be established in flow-through dialysis cells or on rotating dialysis membranes.

The overall flux of the substance i with its molar amount n_i from the donor to the acceptor solution can be described according to eqn [17]:

$$J_i = \frac{dn_i}{dt} = kF\left(\beta_{i,D}c_{i,D} - \beta_{i,A}c_{i,A}\frac{K_{AM}}{K_{DM}}\right) \qquad [17]$$

where $\beta_{i,D}$ and $\beta_{i,A}$ are the fractions of the substance i in the donor and in the acceptor solutions respectively, that can permeate through the separation membrane. K_{DM} and K_{AM} are the distribution constants between the donor solution D and the membrane M and between the acceptor solution A and the membrane, respectively. The overall mass transfer coefficient k can be derived from eqn [18]:

$$\frac{1}{k} = \frac{1}{k_D}\left(\frac{k_D\beta_D}{k_D\beta_D + k'_D(1-\beta_D)}\right) + \frac{1}{k_M K_{DM}} + \frac{K_{AM}}{k_A K_{DM}}\left(\frac{k_A\beta_A}{k_A\beta_A + k'_A(1-\beta_A)}\right) \qquad [18]$$

where $1 - \beta_D$ is the rejected fraction of substance i, $1 - \beta_A$ is the corresponding fraction that is trapped in the acceptor solution, and k_D, k_M and k_A are the mass transfer coefficients of the permeating fractions of substance i for the donor, the membrane and the acceptor phases, respectively. k'_A and k'_D are the mass transfer coefficients for the so-called inactive form of substance i, which cannot permeate the membrane. In many cases the mass transfer across the phase boundary is to be considered additionally, e.g. for homogeneous membranes, supported liquid membranes (SLM) and gas-filled microporous membranes. Then the expression shown in eqn [19] should be added to the right term of eqn [18]:

$$a = \frac{1}{k_{pDM}} + \frac{1}{k_{pAM}}\frac{K_{AM}}{K_{DM}} \qquad [19]$$

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k_{pDM} and k_{pAM} are the phase transfer coefficients from the donor solution into the membrane phase and from there into the acceptor phase, respectively.

From the general equation some cases of analytical interest can be deduced.

Example 1: Dialysis Through Hydrophilic and Microporous Membranes. Because $\beta_D = \beta_A = 1$, $K_{DM} = K_{AM} = 1$ and no phase transfer takes place, eqn [18] can be simplified to eqn [20]:

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_M} + \frac{1}{k_A} \qquad [20]$$

For large concentration gradients $(c_D - c_A)/d_M$ and very intensive stirring in the set-up shown in Figure 1 or in flow-through dialysis cells with high flow-rates the membrane diffusional transport becomes rate-determining particularly for relatively thick membranes with small pores. Eqn [21] then follows:

$$k = k_M \qquad [21]$$

Example 2: Dialysis of Volatile Substances Through Hydrophobic and Microporous membranes. To separate a nonvolatile base B^-, its corresponding volatile acid BH is produced according to the equilibrium:

$$B^- + H^+ \rightleftarrows BH$$

The donor pH value is chosen according to eqn [22] so that there is a 99.9% degree of conversion into the permeable form of the analyte:

$$\beta_{i,D} = \frac{10^{-pH}}{10^{-pH} + K_a} > 0.999 \qquad [22]$$

K_a is the acid-dissociation constant of BH.

The acceptor pH value should be adjusted according to eqn [23] to trap the analyte in its nonvolatile form:

$$1 - \beta_{i,A} = \frac{K_a}{K_a + 10^{-pH}} > 0.999 \qquad [23]$$

Since only the volatile part of the analyte amount can traverse the membrane, it follows that:

$$J_i = kFc_{i,D} \qquad [24]$$

with:

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_M K_{DM}} + \frac{K_{AM}}{k_A K_{DM}} + a \qquad [25]$$

The distribution ratios K_{DM} and K_{AM} are correlated to the concentrations $\beta_{i,D} \times c_{i,1,D}$ and $\beta_{i,A} \times c_{i,1,A}$ of the volatile forms in the donor and in the acceptor solutions, respectively:

$$K_{DM} = \frac{c_{i,g,D}}{\beta_{i,D} c_{i,1,D}} \approx \frac{p_{i,D}}{\beta_{i,D} RT c_{i,1,D}} \qquad [26]$$

$$K_{AM} = \frac{c_{i,g,A}}{\beta_{i,A} c_{i,1,A}} \approx \frac{p_{i,A}}{\beta_{i,A} RT c_{i,1,A}} \qquad [27]$$

The right-hand terms of eqns [26] and [27] are approximations for low partial pressures $p_{i,D}$ and $p_{i,A}$. $c_{i,g,D}$ and $c_{i,g,A}$ are the concentrations of the analyte in the gas phase at the interface between the donor or the acceptor solution, respectively, and the membrane gas phase. For very small partial pressures $p_{i,D}$ and $p_{i,A}$, $K_{AM} \ll K_{DM}$ $(p_{i,D} \gg p_{i,A})$ and without hydrodynamic transport limitations, eqn [18] can be simplified to eqn [28]:

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_M K_{DM}} + a \qquad [28]$$

For fast-flowing donor solutions with $1/k_D \to 0$ the mass transport is determined by the gas diffusion through the membrane, the partial pressure of the analyte in the donor solution and the phase-transfer resistances. The partial pressure of the volatile analyte can be increased by decreasing the partial pressure of the water using high ionic strengths in the donor solution. For highly volatile analytes, thin and highly porous membranes, and fast-flowing solutions, the overall mass transport is controlled by the phase transfer resistance $(k = 1/a)$.

Reverse osmosis The driving force of reverse osmosis is the difference between the outer pressure p_h and the osmotic pressure difference π. The mass transfer can be described according to eqn [29]:

$$J_L = PF(p_h - f_R \pi) \qquad [29]$$

where J_L is the mass flux of the solvent through the separation membrane and P is the water permeability of the membrane. The osmotic pressure difference is multiplied by the reflection coefficient f_R, which is a measure of the solute rejection by the membrane. During the enrichment process in the donor solution the osmotic pressure difference π increases. The driving force decreases. When the rejection is sufficiently high, the reflection coefficient f_R approximates to unity. The rejection ratio is

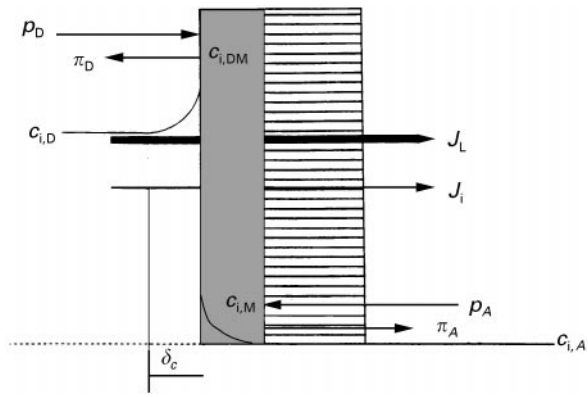

Figure 4 Reverse osmosis with concentration polarization on the asymmetric separation membrane. J_i, mass flux of the solute; p_D, outer pressure from the donor solution; p_A, outer pressure from the acceptor solution; π_D and π_A, osmotic pressures of the donor and the acceptor solution respectively; δ_c, thickness of the polarization layer; $c_{i,D}$, solute concentration in the donor solution; $c_{i,DM}$, solute concentration on the membrane; $c_{i,M}$, solute concentration in the separation membrane. See text for further explanation.

defined by eqn [30]:

$$R = 1 - \frac{c_{i,A}}{c_{i,D,0}} \qquad [30]$$

where $c_{i,A}$ is the solute concentration in the filtrate, and $c_{i,D,0}$ is the initial concentration in the donor solution. The rejected solutes accumulates on the membrane surface (**Figure 4**). This is the so-called concentration polarization phenomenon, which can be described approximately according to eqn [31]:

$$J_L = k_L \cdot \ln[(c_{i,DM} - c_{i,A})/(c_{i,D} - c_{i,A}) \qquad [31]$$

where $c_{i,DM}$ is the solute concentration on the membrane surface and k_L is the mass transfer coefficient.

The concentration up to the saturation level will cause the precipitation of the solute. The precipitated solute forms a secondary layer on the membrane, which reduces the solvent mass transfer J_L. Therefore the concentration polarization must be reduced by a forced convective flow.

The analytical usefulness is based on the high enrichment factor E, which can be achieved following by eqn [32]:

$$E = \frac{c_{i,D}}{c_{i,D,0}} = \frac{V_{D,0}}{V_{D,0} - V_A} \qquad [32]$$

where $V_{D,0}$ is the initial volume of the donor solution.

Geometric Aspects

The geometric shape and extent both of the donor and the acceptor chambers is decisive for the effectiveness and time of the entire separation process. The geometry has to be adapted to the particular analytical task (**Table 1**). To minimize the separation time the thickness of the donor solution layer should be as thin as possible. The ratio of the membrane exchange area to the donor solution volume should be maximized. To maximize the enrichment factor for dialysis with enhanced selectivity the volume ratio between the donor solution and the acceptor solution has to be maximized.

In this respect, thin hollow-fibre membranes are especially useful both for enrichment and purification procedures. Thin-layer chambers with flat membranes are also useful and enable a greater variety of different membrane materials to be used. The miniaturization of the membrane exchange area up to the micro or the ultramicro scale enables reproducible sampling from quiescent or slowly flowing solutions to be performed. This is of great importance for *in vivo* sampling with microdialytic probes.

Figure 5 shows frequently used hollow-fibre and flat-membrane set-ups. Table 1 summarizes the most useful procedures for dialysis.

The Separation Membrane

The dialytic transport across thin membranes can be described in eqn [33]:

$$J_i = \frac{dn_i}{dt} = k_M F(c_{i,MD} - c_{i,MA}) \qquad [33]$$

$c_{i,MD}$ and $c_{i,MA}$ are the solute concentrations in the membrane at the interfaces with the donor and the

Table 1 Dialysis procedures

Objectives in a microanalytical scale	*Donor solution*	*Acceptor solution*
Purification	Quiescent or slowly flowing, small sample volume	Flowing or stirred, large volume
Enrichment	Flowing or stirred, large sample volume	Slowly flowing or gently stirred, small volume
Reagent addition	Stirred or flowing, large reagent volume	Quiescent or slowly flowing, small volume
Separation	Quiescent or slowly flowing, small sample volume	Quiescent or slowly flowing, small volume

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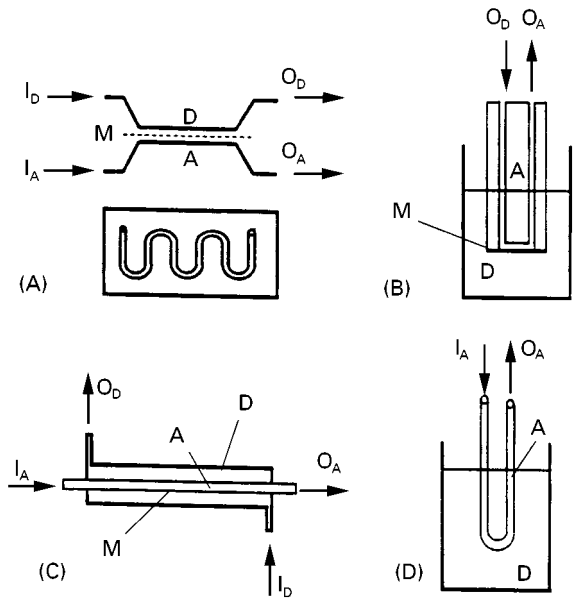

Figure 5 Frequently used dialysis set-up: (A) meander cell with a flat membrane, (B) dialysis probe with a flat membrane M, (C) hollow fibre membrane cell, (D) hollow fibre dialysis probe. I_D, I_A, inlets to the donor and the acceptor chamber; O_A, O_D, outlets from the acceptor and the donor chamber.

acceptor solutions, respectively. Linear concentration gradients can be assumed in thin membranes.

The separation membrane should be considered particularly with regard to selectively but also with regard to the overall mass transfer kinetics. The membrane material determines the transport mechanism, which influences the selectivity of the separation process in particular. **Table 2** gives an overview about the most important membrane materials and the dominant transport mechanisms. Classic dialysis through microporous membranes causes a loss of sensitivity with respect to the following detection or determination procedure. So-called selective dialysis across gas-filled membranes or SLMs enables an analyte enrichment to be performed. The selectivity of the SLM technique can be enhanced by the addition of selectively reacting ligands to the liquid membrane phase. When charged ions are complexed and transported through these membrane systems electroneutrality must be maintained. In many cases ion pairs with selected counter ions are transported through the membrane. When the ligand is dissolved in the liquid membrane phase and the counter ion cannot transverse the membrane the analyte ion transport is coupled with a back-diffusion of an ion with the same electric charge. A similar situation can be found in ion-exchange membranes, which are used to enrich ions by Donnan dialysis.

Gas dialysis through hydrophobic and microporous membranes is a fast transport process compared with the other transport mechanisms. The diffusion constants in the gas phase are several orders of magnitude greater than in liquid and solid phases. The selectivity of the membrane transport is determined by the ratio of the partial pressure p_i of the analyte to the total pressure p in the membrane pores. In small pores the condensation and adsorption kinetics of the gases also have to be taken into account.

Gas dialysis across homogeneous membranes is generally more selective. The different solubilities of the gases in the membrane material are additional selection factors. The mass transport rate is considerably smaller than those in microporous membranes.

Applications

Dialysis

Dialysis is mainly used in flow analytical methods to purify, dilute and condition sample solutions. It can also be used to add reagents.

Table 2 Membrane transport and selectivity

Membrane material	*Transport mechanisms*	*Factors which determine the selectivity*
Hydrophillic and porous	Diffusion through micropores ($k_M = D_m\varepsilon/\zeta d_M$)	Sieve effect
Hydrophobic and porous membranes, filled with an organic solvent	Diffusion through micropores	Solubility and sieve effect
As before, but with selective ligands in the solvent	Diffusion through micropores	Solubility, complexing and sieve effect, co-ion transport
Hydrophobic and gas-filled porous membranes	Gas diffusion and flow	Volatility
Ion exchange membranes	Retarded diffusion through micropores	Ion exchange and Donnan exclusion
Homogeneous and hydrophobic membranes	Solvation and diffusion of gases and hydrophobic solutes with small molecular masses	Solubility in the membrane material

ε, Membrane porosity; ζ, membrane tortuosity; d_M, membrane thickness; D_m, diffusion coefficient.

The dialysis module can be placed prior to or in the sample insertion unit, between the sample insertion unit and the reaction/separation zone and also into the detector zone. Figure 5A shows a typical flow-through dialysis cell, which is inserted in many online configurations with liquid chromatography (LC) and flow injection analysis (FIA), e.g. as shown in **Figure 6**. In Figure 6A the dialysis cell is working continuously. The acceptor stream is connected to the injection valve, which adds the prepurified sample into a nonsegmented carrier flow stream. This configuration is frequently used in LC systems. The sample substances are continuously separated from higher molecular weight substances, precipitations and microorganisms. Therefore dialysis is useful to prevent blocking and prolong the lifetime of the separation column. The continuous dialytic sample pretreatment opens up an effective way to use FIA systems for the online process monitoring of animal cell cultures and other industrial bioprocesses. In many cases food, clinical and environmental samples can be analysed without cumbersome offline sample pretreatment. To circumvent the increased detection limit, which is caused by the inherent dilution, the dialysis cell can be used as a flow-through reactor, in which the analyte is trapped as a more sensitively detectable derivate. The acceptor stream can be stopped for different times to control the reaction time. The separated analytes, e.g. phenol derivatives or aflatoxins, can also be reconcentrated on a solid-phase extraction column, which is inserted into the sampling loop of the injection valve. Also highly specific preconcentration columns, e.g. with immobilized antibodies, can be used.

In Figure 6B the dialysis membrane is contacted only during short concentration impulses with the sample solution. The probability of membrane fouling and clogging is decreased considerably. The sample solution is precisely diluted. This pulsed FIA dialysis is frequently used to adapt ion-selective electrodes, biosensors and miniaturized enzyme reactors to biological sample matrices.

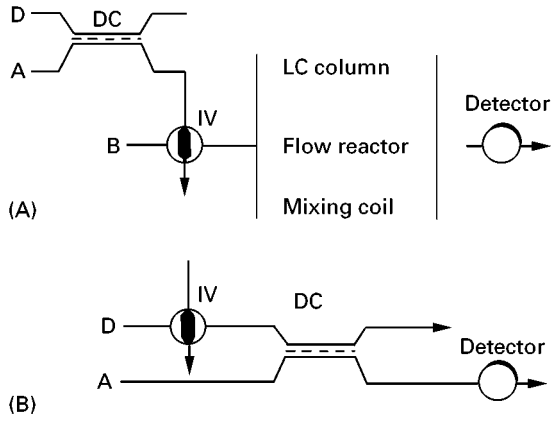

Figure 6 Continuous (A) and pulsed dialysis (B) in flow analytical set-ups. IV, injection valve; DC, dialysis cell; B, carrier solution. See text for further explanations.

A very promising and expanding field of application was opened up by the so-called microdialysis technique. Miniaturized dialysis probes with tip diameters smaller than 1 mm are implanted into different tissues of living animals for sampling low molecular weight substances from the tissue fluid. The low molecular weight analytes are separated across small membrane (cellulose acetate, cut-off 1000-60 000 Da) windows into a flowing acceptor stream, as shown in Figure 5B. The enrichment factor is controlled by the flow rate (0.5–25 $\mu L\,min^{-1}$). The microdialysis probes are coupled online to microcolumn LC systems, to capillary FIA set-ups and recently also to capillary electrophoresis devices. In many cases the separated substances, e.g. lactate and glucose, are converted by enzymes which are dissolved together with the cofactors and cosubstrates in the acceptor solution.

Donnan Dialysis

Donnan dialysis across ion exchange membranes is widely used as an efficient suppression technique in ion chromatography. When a cation exchange membrane separates the eluent, which is an aqueous Na_2CO_3 solution, from a reservoir of strong acid, protons are transported into the eluent. Since the membrane is impermeable to anions, the cations from the eluent must diffuse simultaneously into the suppressor reservoir. The chromatographically separated anions are combined with completely dissociated acids, which have a high equivalent conductivity. The CO_3^{2-} ions are converted to the weakly dissociated carbonic acid. In cation chromatography the eluent, e.g. aqueous hydrochloric acid, has to be suppressed. Therefore an anion exchange membrane is used to separate the eluent from a sodium hydroxide suppressor solution. The anions of the eluent are replaced with hydroxide ions to increase the conductivity in the separation peaks and to suppress the eluent conductivity by neutralization to water. Donnan dialysis across ion exchange membranes can also be used to neutralize strong alkaline and acid samples in an online sample pretreatment for ion chromatography.

Donnan dialysis is also used to enrich low molecular weight ions. When a cation exchange membrane separates a high ionic strength solution from a low ionic strength sample solution, cations are transported from the high ionic strength solution to the

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Table 3 Enrichment and sample pretreatment by Donnan dialysis (Cox (1992) and cited references)

Analyte	*Enrichment factor*	*Detection*
Cations		
Pb(II), Cd(II), Tl(I)	> 100	FAAS
Cd(II)		DPASV
Cu(II)	> 100	FAAS
Cu(II), Zn(II)		ICP-AES
Ca(II)	22	FAAS
Fe(II), Ni(II), Cr(III)	40–80	ICP-AES
Co(II), Cd(II), Mn(II), Cu(II), Ni(II)	80–1000	IC
La(III), Nd(III)	50	ICP-AES
Anions		
AsO_4^{3-}, PO_4^{3-}	5–10	CSV
Cl^-, NO_3^-, SO_4^{2-} PO_4^{3-}	15	IC
Pyruvate, chloroacetate	5–10	V

IC, ion chromatography; FAAS, flame atomic absorption spectrometry; ICP-AES, inducutively coupled plasma-atomic emission spectrometry; ASV, anodic stripping voltammetry; DPASV, differential pulse ASV; CSV, cathodic stripping voltammetry; V, voltammetry.

low ionic strength solution. Since the membrane is almost impermeable to anions, cations from the dilute solution must diffuse back to the more concentrated solution to maintain the electroneutrality. Anions can be analogously separated by means of an anion exchange membrane.

Ions from dilute solutions, e.g. ground and drinking water samples, can be enriched into high ionic strength solutions with volumes which are smaller than the sample volume. The acceptor solutions can be adapted to whatever determination procedure is to be used. Both flat and tubular ion exchange membranes are used, as shown in Figure 5A,B and D.

Tubular ion exchange membranes with a small inner diameter are particularly useful because of their high surface area to internal volume ratios. Such concentrators can readily be combined with flow analytical set-ups, e.g. flow injection analysis-atomic absorption spectrometry (FIA–AAS) and ion chromatography (IC) systems.

Because of the high osmotic pressure difference between the donor and the acceptor solution and the porosity of the ion exchange membranes a slow water flow takes place, which can be neglected in many analytical applications (**Table 3**).

It should be noted that the interaction between the diffusing ions and the fixed counterions in the membrane retards the diffusion, which can be accelerated by an alternating electric field with a frequency around 1 MHz. Multiply electrically charged ions, e.g. Mg^{2+} and Al^{3+}, decrease the interaction between the sample cations and the fixed counterions, whereby the diffusional transport of the sample cations is accelerated.

Selective Dialysis Across Solid and Liquid Membranes

Selective dialysis is defined here as a separation of substances from an aqueous donor phase into an aqueous acceptor phase, the phases being separated by solid and liquid membranes. The analyte transport through such membranes is based on a solvation/diffusion mechanism in a lipophilic phase. The liquid membranes have to be supported by a microporous and hydrophobic layer to enable practical applications to be performed. Again the basic set-up of the flow separation cells shown in Figure 5 can be used to apply these membranes for separation procedures that can be coupled online to LC, gas chromatography (GC) and FIA set-ups.

Thin silicon rubber membranes can be used to separate e.g. phenols and chlorphenols in a 'push–pull' procedure. The sample solution is acidified to shift the chemical equilibrium to the nondissociated phenol/chlorphenol species, which are dissolved in the silicon membrane. The phenol molecules are trapped as phenolate ions in an alkaline acceptor solution. The maximum enrichment factor is determined by the pH values in the donor and the acceptor solution.

Nonpolar organic substances can also be separated from a sample donor solution into an acceptor solution, but the enrichment factor can only be increased to values greater than 0.5 by addition of an organic solvent to the acceptor solution.

The SLMs have the advantages of faster membrane transport and easier modification of the liquid phase, which determines the transport mechanism and the separation selectivity. Dialysis across SLMs has a wide and growing field of application in

Table 4 Applications of supported liquid membranes

Analytes	*Conversion with*	*Membrane transport*	*Trapping by*	*Detection*
Mode A				
Alcohols		*n*-Heptane, supported by microporous PTFE		GC, LC, SnO_2-sensor
Mode B				
Amines[a]	OH^-	*n*-Decane, supported by microporous PTFE	H^+	GC, LC, ph
Phenols	H^+	*n*-Dodecane, supported by microporous PTFE	OH^-	LC, GC, ph
Carboxylates	H^+	*n*-Nonane, supported by microporous PVDF	OH^-	LC, ph
Thiolates	H^+	*n*-Dodecane, supported by PVDF	OH^-	a, GC
Mode C				
Cu(II)[b]	PAR	*n*-Pentane, which contains di-2-ethyl-hexylphosphoric acid and is supported by microporous PVDF	H^+	ph
Pb(II)[c]	Anions	Phenylhexane, which contains bis(1-hydroxyheptyl-cyclohexano)-18-crown-6, supported by microporous PTFE	EDTA	AAS

[a]Jönsson JA, Lövkvist P, Audunsson G and Nilve G (1993) Mass transfer kinetics for analytical enrichment and sample preparation using supported liquid membranes in a flow system with stagnant acceptor liquid. *Analytica Chimica Acta* 277: 9–24.
[b]Barnes DE and Van Staden JF (1992) Flow injection analysis in the evaluation of supported liquid membranes. *Analytica Chimica Acta* 261: 441–451.
[c]Izatt RM, Bruening RL, Bruening ML *et al.* (1989) Modelling diffusion – limited, neutral – macrocycle – mediated cation transport in supported liquid membranes. *Analytical Chemistry* 61: 1140–1148.
a, amperometric: AAS, atomic absorption spectrometry; EDTA, ethylenediaminetetraacetic acid; GC, gas chromatography; LC, liquid chromatography; PAR, 4-(2′-pyridylazo)resorcinol; ph, photometric; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride.

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environmental, food and clinical analysis. **Table 4** summarizes some examples of application. Three modes of selective separation are used:

1. The extraction of a hydrophobic substances into the supported organic liquid phase and the following back-extraction into the aqueous acceptor stream.
2. 'Push–pull' separation. The analyte is converted into a membrane-soluble substance, which diffuses through the membrane and is trapped as a substance that is insoluble in the membrane.
3. Co-ion mediated transport on the basis of a carrier substance which is dissolved in the liquid membrane phase. The carrier molecules take up the analyte molecules or ions, whereby a hydrophobic complex or an ion-pair is formed.

Gas Dialysis

Gas dialysis can also be used for FIA procedures and other flow analytical methods to enhance their selectivity. The configurations shown in Figure 5 can be used to separate and enrich volatile or nonvolatile analytes, which can be converted into a volatile substance. **Table 5** gives an overview of the applications of the gas dialysis technique to determine inorganic substances.

The application range can be extended to volatile and water-soluble organic compounds, e.g. lower alcohols (methanol, ethanol, propanol), formaldehyde, acetaldehyde, acetone, ethylene oxide, propylene oxide, ethyl acetate. Several nonvolatile species. e.g. acetate, propionate, can be separated after acidification. Gas dialysis membranes can separate aqueous solutions with very different pH values and ionic strengths, which enables also extreme sample matrices to be adapted to originally unsuitable detection procedures. Microporous PTFE or polypropylene membranes are used in most cases. However, it should be noted that, for example, surfactants and many water-soluble organic compounds can be adsorbed on the membrane surface, which then becomes increas-

Table 5 Applications of gas dialysis

Analyte	*Conversion to*	*Trapping as or by*	*Detection*
Without conversion			
ClO_2, Cl_2, Br_2, I_2		A colour or chemiluminescence reaction or reduction	a, ph, c, pot
NO, NO_2		Oxidation to NO_3^-	pot (ISE)
N_2H_4		Oxidation	a, ph, c
Conversion by acid–base reaction			
CN^-	HCN	CN^-, $Ag(CN)_2^-$	c, pot (ISE)
SCN^-	HSCN	SCN^-, colour forming reaction	pot, ph
CO_2, HCO_3^-, CO_3^{2-}	CO_2	HCO_3^-	c, pot (ISE), ph
NH_3, NH_4^+	NH_3	NH_4^+, colour forming reaction or oxidation	c, pot (ISE), pH ph, ch, a
NO_2^-	NO	NO_2^-, NO_3^- or colour forming reaction	ph, pot (ISE)
H_2S, HS^-, S^{2-}	H_2S	S^{2-}	pot (ISE), a, c ph
HSO_3^-, SO_3^{2-}	SO_2	SO_2, SO_4^{2-} or colour forming reaction	c, ph
F^-	HF	F^-	pot (ISE)
Conversion by redox reactions			
Cl^-, OCl^-, ClO_2^-, ClO_3^-, Br^-, BrO_3^-, I^-	Cl_2, Br_2, I_2	I^-, Br^- and I^- or Cl_2, Br_2, I_2	pot (ISE), a

a, amperometric: c, conductometric: ch. chemiluminometric: ISE, ion selective electrode: ph, photometric; pot, potentiometric.

ingly hydrophilized. Water penetrates into the membrane pores and changes the mass transfer coefficients considerably with time. In some of these situations homogeneous membranes, e.g. different silicone rubber membranes, can be used to circumvent such interferences. Silicone rubber membranes are permeable to hydrogen sulfide, hydrogen cyanide, carbon dioxide and many volatile organic compounds.

Osmosis and Reverse Osmosis

Diluted sample solutions can be concentrated by both osmosis and reverse osmosis. The concentration process is based on a pressure gradient over a membrane, which rejects the analyte molecules. High molecular weight substances are already rejected by ultrafiltration membranes. But the typical application of reverse osmosis is the separation of low molecular weight substances from aqueous solutions to purify the water or to concentrate the substances which are to be determined.

To concentrate transition and heavy metal ions from dilute aqueous solutions by osmosis the sample solution is separated from a high ionic strength solution by a membrane which is permeable only to the water. An osmotic pressure is built up, which then propels the water into the acceptor (filtrate) solution and concentrates the donor solution. In a thin-layer flow-cell, which is similar to the cell shown in Figure 5A and has a mechanically supported separation membrane (reverse osmosis membrane of cellulose triacetate) preconcentration factors of up to 8–10 for copper(II), cadmium(II), manganese(II), nickel(II) and zinc(II) can be achieved in a countercurrent flow regime.

To implement reverse osmosis, an outer pressure (Figure 2) is applied to propel the water through the membrane. An interesting practical aspect is the possibility of reducing the necessary outer pressure by an osmotic pressure difference which has the same direction. This is implemented by high ionic strength acceptor solutions.

The concentration factor E (eqn [32]) increases considerably with increasing reflection factors (eqn [29])). Highly diluted sample solutions can be concentrated to values that can be determined with the available determination methods. The sample solution can be concentrated up to the precipitation of the solute. Then an additional filter layer is used, which can be exchanged and directly analysed, e.g. by X-ray fluorescence spectrometry. Transition metals could be analysed in drinking water up to the microgram per litre level. Organic contaminants, e.g. chlorobenzene and phenols in alkalized sample solutions, could also be concentrated by reverse osmosis. After this preconcentration traces of the contaminants could be analysed by LC and GC after their redissolution.

Further Reading

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Ultrafiltration

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Introduction

Ultrafiltration (UF) is a filtration process that employs a membrane to fractionate liquid mixtures containing molecules that range in size from about 1000 daltons in molecular weight to 500 000 daltons. The membrane, made of either polymeric or inorganic materials, is a semipermeable barrier containing pores of a certain size distribution that are used to retain or 'reject' components of the feed mixture that are larger than the rated pore size while allowing molecules that are smaller than the pores to pass through the membrane. This separation process is very simple (**Figure 1**) involving only the pumping of fluids. The membrane is assembled in a particular configuration and placed in a module, and the feed stream is pumped through the module over the membrane surface in a cross-flow mode. The pressure forces solvent (e.g. water) and solute molecules smaller than the pores on the membrane surface through the membrane into the 'permeate' stream while larger solutes are rejected and retained in the 'retentate' stream. The retentate is recycled through the module until the required degree of purification, separation or concentration is achieved.

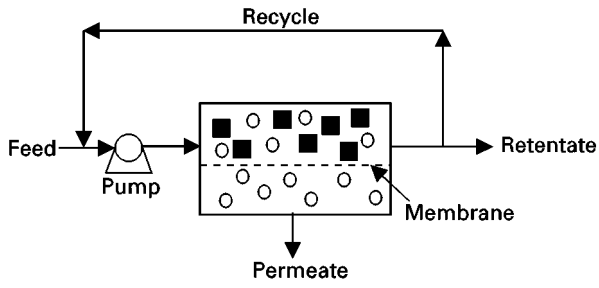

Figure 1 Cross-flow ultrafiltration. Particles in the feed that are larger than the rated pore size of the membrane are retained in the retentate stream while smaller particles pass through into the permeate. (Adapted from Cheryan (1998) with permission from Technomic.)

Ultrafiltration is similar in concept to other pressure-driven membrane processes such as microfiltration, nanofiltration and reverse osmosis. However, as shown in **Figure 2**, the size range of the solutes that are retained by each membrane is different. Reverse osmosis (RO) membranes are designed to retain all components except for the solvent (e.g. water). It is essentially a concentration process. Owing to the osmotic pressure of the solutes retained by RO membranes, pressures needed to operate RO systems are typically 30–60 bar (450–900 lb in^{-2}). Nanofiltration (NF) membranes have slightly larger pores and are designed to allow monovalent salts such as sodium chloride to pass through, but retains divalent salts, disaccharides and dissociated organic acids. Pressures are usually lower, about 15–25 bar. Microfiltration (MF) membranes retain components that are in suspension or in colloidal form, and is essentially a clarification process. Pressures are usually 1–4 bar.

Ultrafiltration, on the other hand, is designed to retain macromolecules and other solutes in the size range of 1–50 nm, or with equivalent molecular weights of 1000 to 500 000 daltons. It also operates at low pressures (2–6 bar) and can simultaneously act as a concentration, purification and fractionation process, depending on the components in the feed and the membrane properties. It has several advantages over other separation or concentration techniques. Unlike freeze concentration or evaporation, there is

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